BATCH ADSORPTION OF AMOXICILLIN ON COCONUT SHELL ACTIVATED CARBON

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BATCH ADSORPTION OF AMOXICILLIN ON COCONUT SHELL ACTIVATED CARBON

by

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Danial Syakirin

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LIST OF EQUATIONS

LIST OF SYMBOLS

Symbol	Description	Unit
a_L	Langmuir isotherm constant	lmg^{-1}
C_e	Equilibrium adsorbate concentration	mgl^{-1}
C_t	Adsorbate concentration at time t	mgl^{-1}
C_0	Initial adsorbate concentration	mgl^{-1}
k_1	Rate constant of pseudo-first-order adsorption	h^{-1}
k_2	Rate constant of pseudo-second-order adsorption	$(hmg)^{-1}$
K_F	Freundlich isotherm constant	$(mgg^{-1})\ (lmg^{-1})1/n$
K_L	Langmuir isotherm constant	(lg^{-1})
1/n	Heterogeneity factor	
K_T	Temkin isotherm constant	
q_e	Amount of adsorbate adsorbed at equilibrium	mgg^{-1}
q_t	Amount of adsorbate adsorbed at time t	mgg^{-1}
V	Volume of solution	l
W	Mass of adsorbent	g

Greek letter

σ	Standard deviation	-

Subscripts

L	Langmuir	-
F	Freundlich	-
T	Temkin	-

LIST OF ABBREVIATION

Symbol	Description
AMX	Amoxicillin
AC	Activated Carbon
DOE	Design of Experimental
UV-VIS	Ultraviolet Visible Spectrophotometer
WW	Wastewater

PENJERAPAN AMOKSISILIN TERHADAP KARBON AKTIVASI TEMPURING KELAPA

ABSTRAK

Oleh kerana spektrum luas terhadap beberapa jangkitan, amoksisilin ialah salah satu antibiotik penisilin komersial yang paling banyak digunakan. Kehadiran mereka dalam ekosistem mungkin dikaitkan dengan isu alam sekitar yang berlaku. Kajian ini bertujuan untuk mengkaji pengaruh dos penjerap, permulaan kepekatan amoksisilin, dan suhu pada pH tetap terhadap penjerapan amoksisilin ke atas karbon teraktif. Eksperimen ini menentukan keadaan kumpulan optimum ialah 10 mg/L kepekatan amoksisilin awal, 2 g dos penjerap, dan 50ºC. Kesan pelbagai parameter pada pemindahan antibiotik amoksisilin antara fasa akueus dan fasa organik telah dikaji, dan ditunjukkan bahawa proses pemindahan kinetik boleh berjaya dimodelkan menggunakan teori dua filem generik pemindahan jisim ke antara muka rata. Menggunakan model pseudo tertib pertama dan pseudo tertib kedua untuk mengkaji kinetik penjerapan amoksisilin pada karbon teraktif tempurung kelapa menunjukkan bahawa penjerapan amoksisilin mengikuti model kinetik tertib pertama pseudo. Di antara tiga model yang diperiksa (Langmuir, Freundlich, dan Temkin), model Langmuir paling baik menggambarkan isoterma penjerapan amoksisilin. Parameter termodinamik ΔG^{o}, ΔH°, dan ΔS° mencadangkan bahawa penjerapan amoksisilin pada karbon teraktif yang diperoleh daripada tempurung kelapa adalah spontan dan endotermik. Kesimpulannya, karbon teraktif tempurung kelapa didapati sebagai penjerap yang berkesan untuk penyingkiran antibiotik amoksisilin daripada air sisa dalam pelbagai situasi.

BATCH ADSORPTION OF AMOXICILLIN ON COCONUT SHELL ACTIVATED CARBON

ABSTRACT

Due to its broad spectrum against a number of infections, amoxicillin is one of the most widely utilised commercial penicillin antibiotics. Their presence in the ecosystem may be linked to impending environmental issues. This study aims to examine the influence of adsorbent dosage, starting amoxicillin concentration, and temperature at a constant pH on the adsorption of amoxicillin onto activated carbon. This experiment determined the optimal batch conditions to be 10 mg/L initial amoxicillin concentration, 2 g adsorbent dose, and 50ºC. The effects of various parameters on the transfer of amoxicillin antibiotic between the aqueous phase and the organic phase were studied, and it was shown that the kinetic transfer process could be successfully modelled using the generic two-film theory of mass transfer to a flat interface. Using pseudo first-order and pseudo second-order models to examine the kinetics of amoxicillin adsorption onto coconut shell activated carbon indicated that amoxicillin adsorption followed a pseudo first-order kinetic model. Among the three examined models (Langmuir, Freundlich, and Temkin), the Langmuir model best described the amoxicillin adsorption isotherm. The thermodynamic parameters ΔG^o, ΔH°, and ΔS° suggested that the adsorption of amoxicillin onto activated carbon derived from coconut shell was spontaneous and endothermic. In conclusion, coconut shell activated carbon was discovered to be an effective adsorbent for the removal of amoxicillin antibiotics from wastewater under a variety of situations.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the overview of this research and significance of antibiotics as the Emerging Contaminants (EC). In general, this chapter summarizes the research background of amoxicillin and application of coconut shell activated carbon as the adsorbent, the problem statement, and the objectives of this final year project.

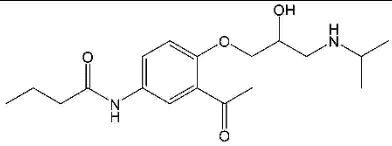
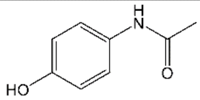
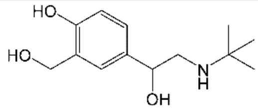
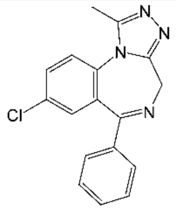
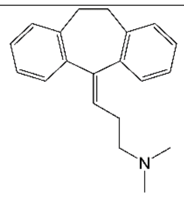
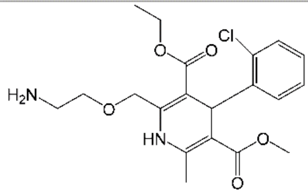
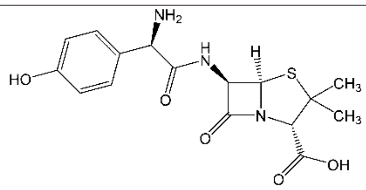
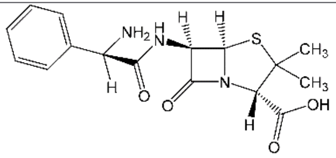
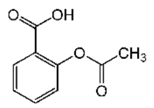
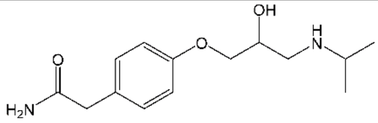
1.1 Emerging Contaminants (EC) involving pharmaceutical antibiotics

Pharmaceuticals have attracted a lot of interest in the last fifteen years as potential bioactive compounds in the environment. In waterbodies, they are classified as Emerging Contaminants (EC). Kümmerer (2009) noted that this is due to the fact that they are still unregulated or are in the process of becoming regulated, despite the fact that directives and legal frameworks have not yet been established. Pharmaceutical antibiotics, which are widely used in human medicine and agriculture around the world, have sparked growing alarm in recent years after it was discovered that they are a class of very toxic pollutants (Balarak, Mostafapour, and Azarpira 2016; Garoma, Umamaheshwar, and Mumper 2010). Little is known about the impacts of pharmaceutical contaminants on flora and fauna, and even less is known about their long-term consequences on humans at ambient quantities. Pharmaceuticals are constantly released into the environment and can be found in minute concentrations (Kolpin et al. 2005), it nonetheless can have an impact on water quality and, as a result, on drinking water sources, the ecosystem, and human health (Sirés and Brillas 2012; Yuan et al. 2009).

On a global scale, there are few explicit norms and legislation pertaining to this topic. According to our knowledge, Australia is the only nation to have created drugs in drinking water standards (Pomati 2007). Pharmaceuticals contain an extensive variety of chemical constituents. On the European Union's market alone, about 3000 regularly used medications are registered. Each day, their global population increases. Consequently, developing legislation, maintaining criteria for all of these chemicals, and monitoring their dispersion in the environment is a difficult task, which is made much more difficult by the fact that hundreds of more compounds are registered but rarely used. A German research group recently claimed that over 600 distinct medications are now recognised as pollutants worldwide. **Table 1.1** provides a listing of some of the most widely used medicines, along with their classes, therapeutic applications, and significant physicochemical features.

It was recently proven that pharmaceutical chemicals pose a threat to ecosystems. These pharmaceutically active chemicals are considered pseudo-persistent due to their continual influx into environmental matrices despite their constant breakdown and elimination by diverse mechanisms. This results in the formation of a "complex pharmaceutical pool" in a variety of natural matrices. Once pharmaceutical residues enter water and soil, they are absorbed by plants that thrive in these soils or waters. There have been reports of uptakes in cabbage, cucumbers, corn, carrots, lettuces, and green onions, among others. Since the majority of antibiotics, including Amoxicillin, are poorly digested and absorbed by humans and animals, large portions are eliminated via urine as the unmodified parent molecule. Antibiotic residues regularly identified in soil, surface water, groundwater, and even drinking water (Balarak, Mostafapour, Bazrafshan, et al. 2017). According to Rostamian and Behnejad (2016), the one of the very popular b-lactam antibiotics used to take care of human and animal infections is Amoxicillin (AMX).

Table 1.1 Commonly Used Pharmaceuticals, Their Classes, Therapeutic Applications, Physicochemical Properties, and Structures (PubChem 2004)

Pharmaceuticals (CAS number)	**Class/therapeutic application**	**Chemical formula (Mol. Wt. in g/mol)**	**pKa**	**logK$_{ow}$**	**Predicted CEC[a] (ng/L)**	**Structure**
Acebutolol (37517-30-9)	β-blocker/Anti-hypertensive/ Human use	$C_{18}H_{28}N_2O_4$ (336.432)	13.8	1.53		
Acetaminophen (Paracetamol) (103-90-2)	Analgesic/ Anti-pyretic/ Human and veterinary use	$C_8H_9NO_2$ (151.165)	9.38	0.46	2.4E+07	
Albuterol (Salbutamol) (18559-94-9)	Bronchodilator/ Human use	$C_{13}H_{21}NO_3$ (239.315)	10.3	0.64	27669	
Alprazolam (28981-97-7)	Benzodiazepine/ Anti-anxiety drug/Human use	$C_{17}H_{13}ClN_4$ (308.769)		2.12	57	
Amitriptyline (50-48-6)	Antidepressant/ Human use	$C_{20}H_{23}N$ (277.411)	9.4	4.92	48	
Amlodipine (88150-42-9)	Calcium channel agents/Antianginal agents/Human use	$C_{20}H_{25}ClN_2O_5$ (408.879)	9.4	3.00	7003	
Amoxicillin (26787-78-0)	Antibiotic/ Antibacterial/ β-lactums/ Human applications	$C_{16}H_{19}N_3O_5S$ (365.404)	3.2, 11.7	0.87	7.4E+06	
Ampicillin (69-53-4)	Antibiotic/ Antibacterial/ β-lactums/Human applications	$C_{16}H_{19}N_3O_4S$ (349.405)	2.5, 7.3	1.35	12191	
Aspirin (Acetylsalicylic acid) (50-78-2)	Analgesic/ Antipyritic/Human and veterinary use	$C_9H_8O_4$ (180.159)	3.49	1.19	3.4E+08	
Atenolol (29122-68-7)	β-blocker/Anti-hypertensive/ Human use	$C_{14}H_{22}N_2O_3$ (266.341)	9.6	0.16	792332	

Active pharmaceutical ingredients are substances that are pharmacologically active, resistant to degradation, persistent in aqueous systems, toxic to organisms, and have a detrimental impact on human health. According to (Patel et al. 2019), Diclofenac, carbamazepine, clarithromycin, ketoprofen, clofibric acid, and amoxicillin had poor clearance (2050% mean removal efficiencies). Diclofenac, carbamazepine, clarithromycin, ketoprofen, clofibric acid, and amoxicillin had poor clearance (2050% mean removal efficiencies).

Amoxicillin is a broad-spectrum b-lactam antibiotic that belongs to the penicillin class and is used in veterinary medicine to treat gastro-intestinal and systemic bacterial infections (De Baere and De Backer 2007; Douša and Hosmanová 2005). Due to its broad spectrum against bacteria, it is also frequently employed in human prescription drugs (to treat bacterial illnesses) and as therapeutic agents (Aksu and Dede 2005). Amoxicillin is also notoriously difficult to degrade, retaining its activity in urine and faeces (Andreozzi et al. 2005; Carlesi Jara et al. 2007).

Wastewater gets released from different types of industries and is a significant source of different heavy metals, dyes, detergents, and other contaminants that can consume dissolved oxygen of accommodating water stream, can alter chemical and biological characteristics of the water, and poses environmental hazards by endangering ecosystems and human health (Aktar 2020). Amoxicillin (AMX) has been detected in several aqueous matrices (WWTP effluents, hospital effluents, river and sea water) and the toxic effects of this compound towards aquatic organisms have been recently reported by (Tran et al. 2016). Currently there are methods to eliminate AMX from Pharmaceutical wastewater with biological, chemical, and physical methods available including biodegradation, advanced oxidation processes (AOPs) and adsorption (Balarak, Mostafapour, Akbari, et al. 2017). Hence, wastewater treatment is prerequisite before its discharge into the ecosystem. Although there are multiple water treatment options are being used frequently, adsorption process is still unrivalled because of its effectiveness, low energy consumption, and easiness to perform; therefore, the versatility of adsorption makes it extensively used while removing contaminants from wastewater (Balarak, Mostafapour, Akbari, et al. 2017).

1.2 Batch Adsorption by Coconut Shell Activated Carbon

1.2.1 Batch Adsorption

Mainly, the adsorption process is used for the removal of a highly toxic or low concentrated compound, which is not readily treated by biological processes (Xu, Cai, and Pan 2013). Even at very low concentrations (less than 1 mg/L), adsorption is regarded as highly effective for removing pollutants from water or wastewater. Depending on the type of adsorbent, this approach is straightforward, adaptable to common chemicals, and has a cheap cost of operation compared to other procedures. Only a small number of papers on antibiotic removal from wastewater using different adsorbents are currently accessible for reference (Adriano et al. 2005; Gao and Pedersen 2005; Khalil, Mortada, and El-Khawas 1984; Zhang and Huang 2007).

Immediately, the batch method is utilised for the adsorption treatment of wastewater. The batch process takes place in a closed system with the optimal amount of adsorbent in contact with the present volume of adsorbate solution. In a closed vessel, revolving stirrers provide agitation for the complete mixing of adsorbent materials and polluted solution. After treatment, effluent of high quality that is recyclable is produced using batch methods that have been meticulously devised as shown in **Figure 1.1**.

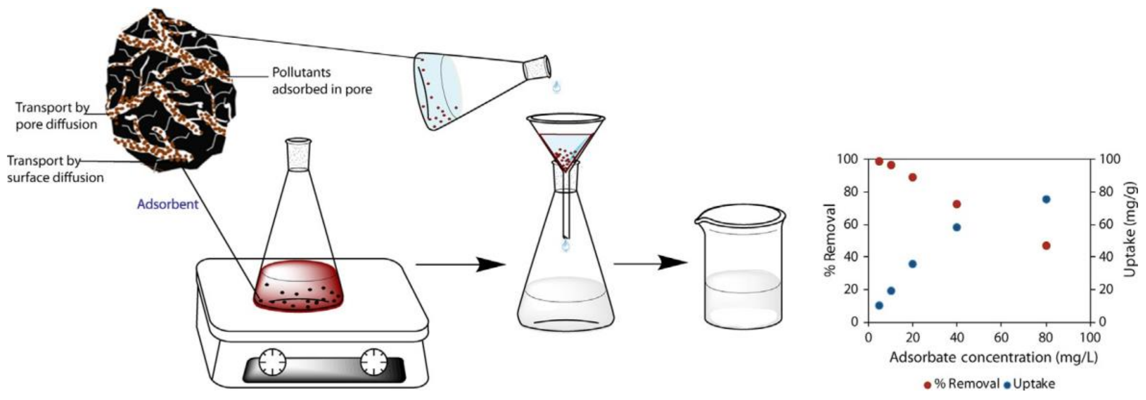


Figure 1.1 Batch Adsorption Process

Moreover, batch adsorption process can be cost effective if low-cost adsorbents are used or regeneration is feasible (Nguyen et al. 2018). Furthermore, the batch adsorption process can also be used for abatement of pollutants at source and quality improvement of industrial and other wastewater Physical techniques remain the most appropriate treatment option and adsorption is among the most efficient of these techniques for removing organic compounds from industrial effluents (Afkhami, Saber-Tehrani, and Bagheri 2010; Thakre et al. 2010). According to (Aktar 2020), adsorption is an effective and inexpensive method for wastewater treatment, as well as it is unaffected by toxicity. So, adsorption an efficient and effective technique for purification of harmful organic compounds from contaminated water and wastewater. A saturated adsorbent is easily separated from a treated stream for regeneration or disposal in an environmentally acceptable way (Kumar, Ray, and Chakraborty 2009).

1.2.2 Activated Carbon as the adsorbent

Activated carbon (AC) is an amorphous, crude form of graphite with a highly porous structure consisting of pores varying in size from the molecular level to obvious crevices and cracks. The surface chemistry, pore architectures, and surface area of activated carbon vary depending on the feedstock and activation conditions (Yuen and Hameed 2009). Activated carbon has been widely used to remove organic contaminants from water and wastewater in industrial scale application. It has high adsorption capacity as well as removal efficiency for certain organic substances. In some application, the removal efficiency can reach 100%. In real application, the adsorption processes using activated carbon are carried out in column mode. However, the major drawback for wastewater treatment utilization comes from economic consideration; the commercially available activated carbons are expensive, rendering its infeasibility for large scale operation (Putra et al. 2009). The main advantage of using activated carbon to remove pharmaceuticals is that it does not generate toxic or pharmacologically active products. According to the literature, activated carbons generally demonstrated a high capacity to adsorb pharmaceuticals which depended on the activated carbon type, pharmaceutical composition, and solution chemistry (Adams et al. 2002; Dutta, Dutta, and Bhattacharya 1999; Fuerhacker, Dürauer, and Jungbauer 2001; Snyder et al. 2007; Yuen and Hameed 2009).

1.3 Problem Statement

In recent years, pharmaceutical antibiotics, which are widely used in human therapy and the agricultural business, have garnered growing concern since they have been proven to be a class of strong pollutants. Since the majority of antibiotics, including Amoxicillin, are poorly digested and absorbed by humans and animals, large portions are eliminated via urine as the unmodified parent molecule. The primary benefit of removing pharmaceuticals with activated carbon is that it does not generate poisonous or pharmacologically active byproducts. In addition, adsorption utilising activated carbon as an adsorbent is the best approach for cleaning because it is environmentally friendly, easy, cost-effective due to its minimal initial investment, and does not create secondary pollutants. Activated carbon is a well-known adsorbent having a porous surface that can increase the contaminant's adsorption due to the high surface area supplied.

Consequently, the purpose of this study is to investigate the adsorption behaviour of Amoxicillin (AMX) onto coconut shell activated carbon at a given pH, while altering other parameters including temperature, initial concentration of AMX, and adsorbent dosage in batch mode. From the obtained experimental data, more analysis is required to analyse the adsorption isotherms, kinetics, and thermodynamics in order to fully comprehend the adsorption process.

1.4 Research Objectives

The objectives of this study are:

i. To study the effect of adsorbent dosage, initial concentration of amoxicillin and temperature at fixed pH on the amoxicillin adsorption onto activated carbon.

ii. To compare the behaviour of amoxicillin adsorption by using adsorption isotherms and adsorption kinetics model.

iii. To study the thermodynamics behind amoxicillin adsorption mechanism.

CHAPTER 2

LITERATURE REVIEW

In previous chapter, the significance of pharmaceuticals as the emerging contaminants (EC) especially amoxicillin and activated carbon as the adsorbent has been discussed. In the view of aforementioned observations, Chapter 2 presents the previous discoveries and reviews available from credible scientific records and references that are related to this final year project topic. This chapter covers the overview of amoxicillin removal technologies, batch adsorption of amoxicillin, and detailed explanation on activated carbon as the adsorbent. Besides, this chapter also presents important concept and equations from adsorption isotherms, adsorption kinetics and adsorption thermodynamics.

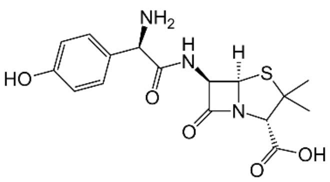
2.1 Amoxicillin

Due to its great bacterial resistance and broad spectrum against a number of pathogens, amoxicillin is one of the most widely used commercial penicillin antibiotics (Maichin, Freitas, and Ortiz 2013; Mohammadi et al. 2015). Its presence in wastewater from pharmaceutical industries and hospital effluents results in unpleasant odour, skin disease, microbial resistance among pathogen organisms, or the death of microorganisms that are effective in wastewater treatment. The resistant bacteria may cause diseases that cannot be treated with standard antibiotics; consequently, amoxicillin wastes must be treated before to disposal (Asmaa Boukhelkhal et al. 2015; Chayid and Ahmed 2015; Zha et al. 2013a). There is a clear necessity to remediate wastewaters containing medicinal compounds.

The amoxicillin (AMX) stands out among other medications in this class of antibiotics. This antibiotic is commonly used for the treatment of bacterial infections in humans and animals (Bago et al. 2011; Michael et al. 2013). In addition, amoxicillin also accumulates through industrial route, where the concentration is usually much higher than that originated from public excretion (Aksu and Dede 2005). Their presence on the ecosystem is potentially linked to future environmental issues. For example, (Pan et al. 2008) recently reported the toxic effects of this compound toward algae Synechocystis sp., mainly by inhibiting its photosynthesis mechanism.

Furthermore, while accumulated within a single organism, i.e., pathogenic bacteria, amoxicillin would increase the pathogen's resistance, necessitating a higher dosage or rendering it incapable of treating traditional infections.(Aksu and Dede 2005). Therefore, the removal of amoxicillin residue from the environment is deemed essential and offers as a compelling case study. Even though amoxicillin removal is expensive, the pharmaceutical industry must treat its wastewater before releasing it into the environment (Putra et al. 2009). The molecular structure and properties of amoxicillin are shown in **Table 2.1**.

Table 2.1: Molecular Properties of Amoxicillin (National Center for Biotechnology Information 2022)

Molecular Structure	Molecular Formula	Molecular Weight
	$C_{16}H_{19}N_3O_5S$	365.4 g/mol

2.2 Amoxicillin Removal Technologies

Numerous approaches, including oxidation processes, have been applied to the removal of antibiotics (Eslami et al. 2016; Jung et al. 2012), membrane filtration (Derakhsheshpoor et al. 2013) and nanofiltration (Karimnezhad et al. 2020), and adsorption (D. Hu and Wang 2016; Kasperiski et al. 2018; Kerkez-Kuyumcu, Bayazit, and Salam 2016; Diana R Lima et al. 2019; Diana Ramos Lima et al. 2019). According to Machado et al., 2011, adsorption is a promising approach because of its high efficiency, reusability of the adsorbent, scalability, short retention duration, and absence of secondary pollutants. In addition to promoting the circular economy, the adsorption process with a suitable adsorbent derived from agro-industrial waste may be an innovative method for removing pharmaceuticals from wastewater. The summary of antibiotics elimination technologies is shown in the **Table 2.2** .

Table 2.2 Summary of antibiotics elimination technologies

Author	Sample Analyte	Method	Note
(Eslami et al. 2016)	Amoxicillin	Oxidation	It was observed that the sulphate radical-based advanced oxidation process (SR-AOP) is an effective and efficient technology for the mineralization of amoxicillin in aqueous solution.
(Jung et al. 2012)	Amoxicillin	Direct UV-C and UV/H_2O_2 photolytic processes	The degradation rate of amoxicillin in both processes fitted pseudo first-order kinetics, and the rates increased up to six-fold with increasing H_2O_2 addition at 10mM H_2O_2 compared to direct photolysis.
(Derakhsheshpoor et al. 2013)	Amoxicillin	Polysulfone nanofiltration membranes	Fabricated membranes had higher flux as well as relatively high AMX separation. Moreover, pH enhancement increased AMX rejection by 85%.
(Karimnezhad et al. 2020)	Amoxicillin	Simultaneous combination of Fenton and nanofiltration processes (NF/FT)	The results indicated that by increasing the pollutant (AMX) concentration, the antibiotic removal efficiency increased for PAN/Goe membrane.

Table 2.3 Summary of antibiotics elimination technologies (cont.)

(Diana Ramos Lima et al. 2019)	Amoxicillin	Adsorption	The use of the adsorbents for treatment of simulated hospital effluents, containing different organic and inorganic compounds, showed excellent removals (up to 98.04% for CCP.600 and 98.60% CCP.700)
(D. Hu and Wang 2016)	Amoxicillin	Adsorption	Adsorption studies were conducted by varying solution pH, contact time, and adsorbent dosages. Adsorption kinetics and isotherms were fitted to different nonlinear models. Quaternized cellulose from flax noil (QCFN) was proven to be a promising and efficient adsorbent for the removal of AMX from aqueous solution.
(Kasperiski et al. 2018)	Captopril	Adsorption	The employment of the ACs for treating simulated effluents, with different emerging contaminants, showed an excellent removal (up to 97.67%). This result is evidence that Caesalpinia ferrea seed pod wastes were a high-efficiency precursor for AC preparation and that such activated carbons could be used for treating hospital effluents containing pharmaceuticals.
(Kerkez-Kuyumcu, Bayazit, and Salam 2016)	Amoxicillin	Adsorption	The results showed the great affinity of the M-GNPs toward the AMX, and the maximum adsorption capacity was found to be 14.10 mg g^{-1}.

2.2.1 Adsorption Process

Adsorption is the method of acquiring molecules on the surface of solids, such as how activated charcoal collects hazardous gases. Figure 2.1 illustrates the fundamental adsorption process concept. When gases or solutes attach to solid or liquid surfaces, adsorption also occurs as a mass transfer mechanism. Due to unbalanced forces, the molecules or atoms on the surface of a solid have excess surface energy, which is known as adsorption. When certain substances come into contact with a solid surface, these unequal pressures cause them to adhere to the surface (H. Hu and Xu 2020).

The majority of pharmaceutical waste is found in rivers and other water sources. This may be owing to the irresponsibility of some enterprises that dump trash into surrounding water streams in an effort to cut capital costs, or to waste leaks of which the company is unaware. In order to eliminate this waste, adsorption on activated carbon has been investigated and implemented in modern companies. Amoxicillin adsorption on chitosan beads has been reported; the kinetics and equilibrium of amoxicillin adsorption on chitosan beads suit the Langmuir model well (Adriano et al. 2005). Recent research into the adsorption of amoxicillin onto bentonite and activated carbon reveals that the adsorption of amoxicillin onto activated carbon plays a crucial role (Putra et al. 2009). Additionally, activated carbon adsorption can eliminate the colour of wastewater.

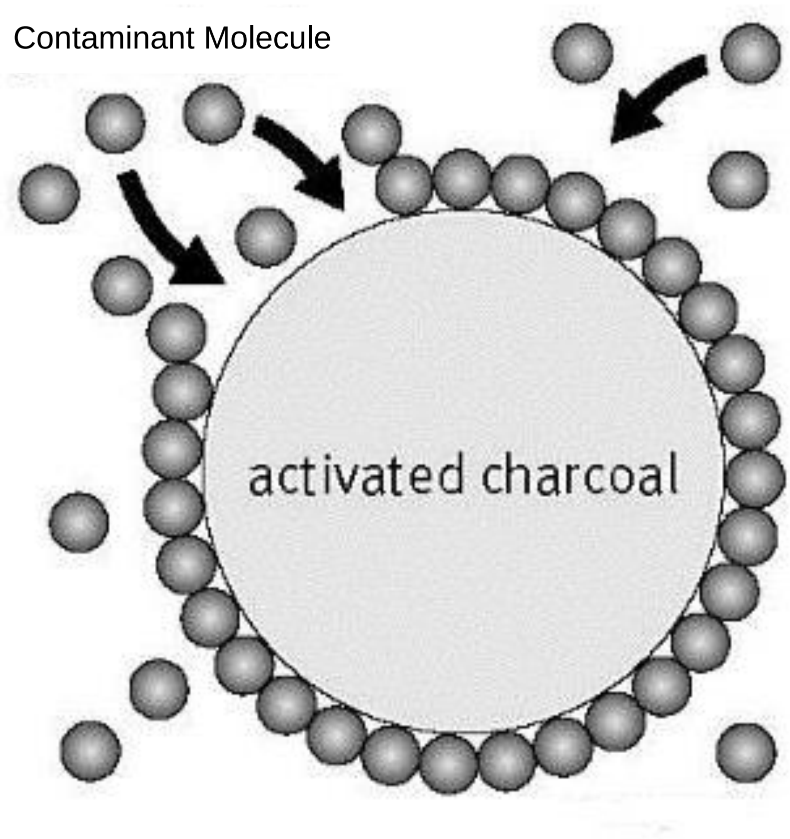


Figure 2.1 General mechanism of adsorption

Physical adsorption (physisorption) and chemical adsorption are the two types of adsorption (chemisorption). Chemisorption can occur due to covalent bonding and electrostatic attraction, whereas weak van der Waals forces govern physisorption. This indicates that chemisorption has stronger forces than physisorption. Since this type of bonding can change the chemical form of the adsorbed molecules, it is irreversible (Aoran and Tsouris 2005). The mechanism of adsorption involving the movement of adsorbate from bulk phase on the surface of adsorbent, followed by the transport of adsorbate into adsorbent and finally, the adsorption of adsorbent occurs. When an equilibrium is altered on the adsorbent surface, desorption occur whereby the adsorbate will release from or through the surface of adsorbent.

2.2.2 Activated Carbon (AC)

Activated carbon is a coarse kind of graphite with a random or amorphous structure that is highly porous across a broad range of pore sizes, from visible to molecular fissures and crevices. According to (Saleem et al. 2019), Activated carbons' pore structures provide significant adsorption. Activated carbons are one of the materials used to remove organic compounds such as EC from wastewater and other water bodies due to this ability. Typically, the surface areas of commercial-grade carbons range from 500 to 1500 m2/g, with some exceeding 3000 m2/g.(Saleem et al. 2019). As per the IUPAC (International Union of Pure and Applied Chemistry), pores are categorized into three types depending on pore size:

Table 2.4 Pore diameters for activated carbon

Type of pores	Diameter	Unit
Macropores	> 50	nm
Mesopores	2 - 50	nm
Micropores	< 20	nm

A considerable amount of the internal surface area is comprised of micropores. Macropores and mesopores are essential for kinetics because they provide access to the carbon particle. On the basis of their applications, they are further subdivided into two subcategories: gas phase and liquid phase, with the former being microporous (pore diameter 2 nm) in granular form (2.36–0.833 mm, or 8/20 mesh size) and the latter being mesoporous (pore diameter 2–50 nm) in powdered form (0.150–0.043 mm, or 100/325 mesh size). Granular and powdered activated carbons have been proven to be effective in wastewater treatment, where they play an important role in decolorization, odour removal, metal recovery, and organics adsorption (Saleem et al. 2019). In larger systems cylinders of activated carbon may also be used to adsorb larger quantities of organic impurities. General mechanism of adsorption using activated carbon is demonstrated in **Figure 2.2 ss**.

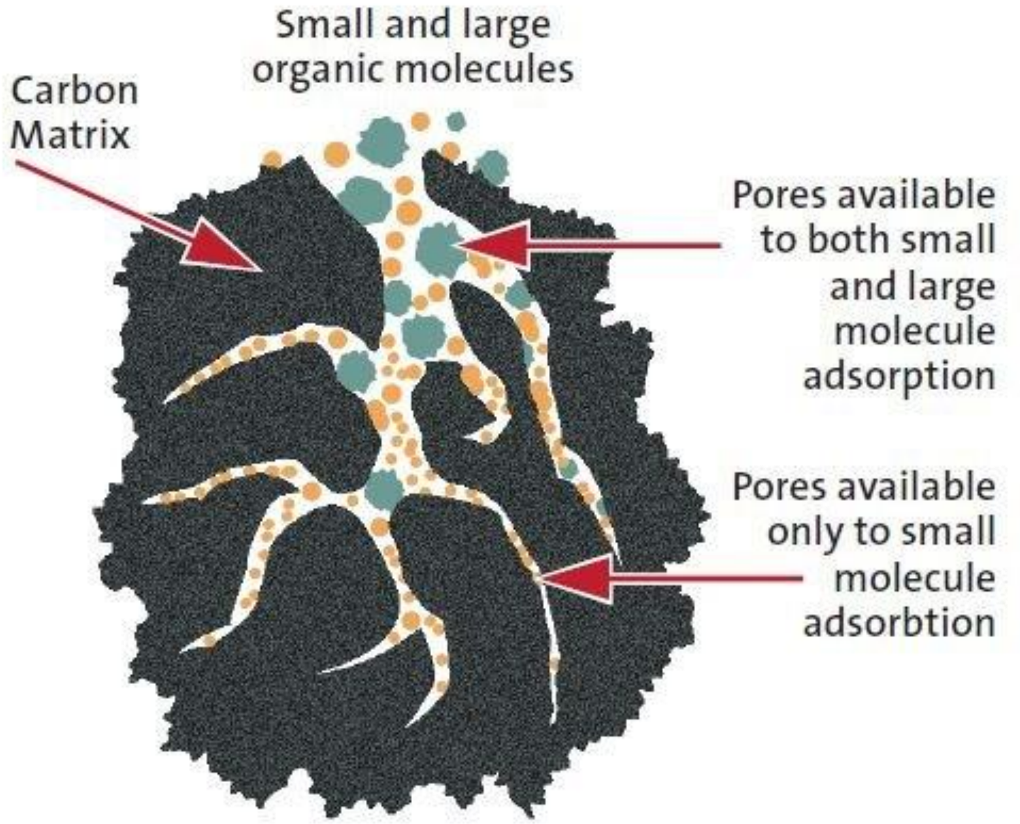


Figure 2.2: General mechanism of adsorption process (Veolia 2021)

2.3 Adsorption Isotherms

Adsorption isotherms are a vital component of the adsorption process. The adsorption isotherm is a graphical representation of the relationship between the amount adsorbed by a unit weight of adsorbent (such as activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium, as well as the distribution of an adsorbable solute between the liquid and solid phases at various equilibrium concentrations (Chilton Ng et al. 2002). Therefore, the adsorption isotherm in this study is an empirical relationship that predicts how much amoxicillin activated carbon can absorb.

2.3.1 Langmuir Isotherm

The Langmuir adsorption model is the most common model for estimating the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a particular temperature. The Langmuir isotherm model posits that the adsorption process occurs at discrete, homogeneous sites on the surface of the adsorbent. According to the assumptions, when a molecule is adsorbed onto a site, other molecules cannot adsorb at that site (Koduru, Karri, and Mujawar 2019). The Langmuir isotherm was constructed on the idea that the adsorption process will only occur at particular homogeneous sites with uniform energy level distribution on the adsorbent surface. Once the adsorbate is bound to the site, no additional adsorption may occur, indicating that the adsorption process is of a monolayer type. Equation 2-1 below can be used to represent Langmuir Isotherm.

Equation 2-1: Langmuir Isotherm Equation

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e$$

where qe is amount of adsorbate adsorbed at equilibrium (mg g^{-1}), Ce is equilibrium concentration of the adsorbate (mg l^{-1}). K_L and a_L are Langmuir isotherm constants (l g^{-1}) and (l mg^{-1}), respectively. For Langmuir, plots of Ce/qe versus Ce give a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the Langmuir constant related to maximum adsorption capacity at monolayer, Q_0 (mg g^{-1}).

2.3.2 Freundlich Isotherm

In contrast to Langmuir, Freundlich assumed that adsorption happens on heterogeneous sites with non-uniform energy level distribution. The Freundlich model describes reversible adsorption and is not limited to monolayer formation (Mall, Srivastava, and Agarwal 2006; C Ng et al. 2002). On heterogeneous surfaces, the Freundlich isotherm can be used to describe adsorption processes. This isotherm defines the surface heterogeneity, exponential distribution of active sites, and their energy. The Freundlich isotherm is depicted by Equation 22-2.

Equation 2-2: Freundlich Isotherm Equation

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$$

where qe is amount of adsorbate adsorbed at equilibrium (mg g^{-1}), Ce is equilibrium concentration of the adsorbate (mg l^{-1}). As for Freundlich, a plot of log qe versus log Ce enables the determination of constant K_F and exponent 1/n. K_F is Freundlich constant (mg g^{-1}) (l mg^{-1})1/n and 1/n is dimensionless heterogeneity factor.

2.3.3 Temkin Isotherm

The Temkin isotherm model considers the impacts of indirect adsorbate/adsorbate interactions on the adsorption process, as well as the assumption that the heat of adsorption is proportional to the adsorbate concentration. (ΔH_s) of all molecules in the layer reduces linearly as surface coverage increases (Nimibofa, Ebelegi, and Donbebe 2017). The Temkin isotherm model seeks primarily to characterise electrostatic interactions in chemical adsorption processes and their related heat of adsorption. Consequently, the isotherm model describes adsorption parameters that suggest the possibility of adsorbent-adsorbate interactions, with less focus on extremely low or high adsorbate concentrations. The Temkin model also implies that the heat of adsorption may drop linearly as the adsorbent surface becomes saturated (Chitongo, Opeolu, and Olatunji 2019). As for Temkin isotherm can be shown in Equation 2-3 below.

Equation 2-3: Temkin Isotherm Equation

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

where qe is amount of adsorbate adsorbed at equilibrium (mg g^{-1}), Ce is equilibrium concentration of the adsorbate (mg l^{-1}). As for Temkin, a plot of qe versus ln Ce enables the determination of constant K_T and b. K_T is Temkin constant.

2.4 Adsorption Kinetics

With a comprehensive understanding of adsorption equilibrium and kinetics, it is possible to identify the adsorbent-adsorbate interactions in the adsorption process. Adsorption kinetics is employed to comprehend the rate that governs the reaction and to establish the optimal circumstances for the process (Vieira et al. 2020). The main kinetic models used recently were pseudo-first order and pseudo-second order (Vieira et al. 2020). These two models are critical for identifying whether physisorption or chemisorption is the method of adsorption. Kinetic modelling gives comprehensive information regarding the sorption mechanism of a solute onto an adsorbent. In this study, the well-known Lagergren kinetic model and the intra-particle diffusion model are utilised to evaluate the chemical reaction as a rate-controlling parameter for the phenol adsorption mechanism. The application of Lagergren-based kinetic models has been elaborated on numerous occasions in the earliest studies (Ahmad, Hameed, and Aziz 2007; Ho 2006).

2.4.1 Pseudo-First Order (PFO)

Because film diffusion is the limiting stage, the pseudo-first-order model implies adsorption occurs via a physisorption mechanism. Non-linear PFO is used to prevent any inaccuracy in estimating k1 parameters. Long ago, the PFO model was considered an empirical model. Equation 2-4 shows the Pseudo-First Order Equation used in this experiment.

Equation 2-4: Pseudo-First Order Equation

$$q_t = q_e(1 - \exp(-k_1 t))$$

Where k_1 = rate constant of pseudo-first order (min^{-1})

2.4.2 Pseudo-Second Order (PFO)

In the majority of published works, the PSO model was utilised to anticipate adsorption experimental data and calculate adsorption rate constants. Similar to PFO, the nonlinear equation is favoured due to the imprecise estimation and calculation of the parameter, k_2. The rate constant of PSO or k_2 is utilised to characterise the equilibrium adsorption rate. Pseudo-Second Order Equation is shown in Equation 2-5 below.

Equation 2-5: Pseudo-Second Order Equation

$$q_t = q_e \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

k_2 = rate constant of pseudo-second order (g/mg min)

2.5 Adsorption Thermodynamics

To evaluate whether the adsorption process is spontaneous or nonspontaneous, thermodynamics analysis is essential. According to (Das and Chowdhury 2011) at a higher temperature, The adsorption procedure becomes more beneficial as the negative value of Gibb's free energy decreases. Due to the increased mobility of adsorbate molecules at high temperatures, the affinity of the adsorbate for the adsorbent increases as the temperature rises.

A rise in the negative value of Gibb's free energy, on the other hand, implies that adsorption is more favourable at lower temperatures. Van's Hoff equation (Das and Chowdhury 2011) is used to study the parameter of thermodynamics in order to investigate amoxicillin adsorption onto activated carbon at different temperature.

Equation 2-6: Gibbs Free Energy

$$\Delta G^{\circ} = -RT \ln K_D$$

Where, $K_D = C_a/C_e$

$\Delta G°$ = Gibb's free energy (KJ/mol)

R = Gas constant 8.314 J/mol.K

T = Temperature (K)

C_a = Equilibrium adsorbate concentration on adsorbent (mg/L)

C_e = Equilibrium adsorbate concentration in solution (mg/L)

When the process changes with temperature, equation above could be further integrated with respect to temperature.

Equation 2-7: Differential equation with respect to temperature

$$\frac{d \ln K_D}{dT} = \frac{\Delta H^{\circ}}{RT}$$

Upon integration and rearrangement,

Equation 2-8: Equation 8 Final Gibb's free energy equation

$$-RT \ln K_D = \Delta H^{\circ} - \gamma RT$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S$$

Enthalpy and entropy can be obtained from the graph of $\Delta G°$ against temperature, T.

CHAPTER 3

METHODOLOGY

This chapter discloses the information on the methods applied in this final year project. It includes the general research flow diagram, Design of Experiment (DOE) and statistical analysis for this study.

3.1 Overview of Research

Overall, this final year project focused on the adsorption of amoxicillin by activated carbon. The experimental design and statistical analysis utilizing Ultraviolet-Visible spectrophotometer to study the calibration curve of amoxicillin, adsorption at different initial concentration, temperature and adsorbent dosage were discussed. **Figure 3.1** shows the overview of the activity of this research.

The experiment Setup will be carried out in Adsorption and Sustainability Laboratory USM. Data analysis will be completed in order to study the adsorption isotherms, adsorption kinetics and adsorption thermodynamics. Report writing will be done after completed the whole experiment and data analysis. Otherwise, the experiment will be repeated if the data collected are not agreeable.